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Synthesis of Highly Crosslinked Temperature-resistant Poly(vinyl ethers) by Free Radical Polymerization

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2,4-Di-(2-vinylloxyethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 3,4-di-(2-vinylloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3,4-di-(2-vinylloxyethoxy)benzylidenecyanoacetate (**4b**), 2,5-di-(2-vinylloxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2,5-di-(2-vinylloxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensation of 2,4-di-(2-vinylloxyethoxy)benzaldehyde (**1**), 3,4-di-(2-vinylloxyethoxy)benzaldehyde (**3**), and 2,5-di-(2-vinylloxyethoxy)benzaldehyde (**5**) with malononitrile or methyl cyanoacetate, respectively. Trifunctional divinyl ether monomers **2**, **4** and **6** were polymerized readily by free radical initiators to give optically transparent swelling poly(vinyl ethers) **7-9**. Polymers **7-9** were not soluble in common organic solvents such as acetone and DMSO due to crosslinking. Polymer **7-9** showed a thermal stability up to 300 °C in TGA thermograms.

Introduction

Electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize readily with electron-poor olefins such as vinylidene cyanide,¹ 2-vinylcyclopropane-1,1-dicarbonitrile,² alkyl acrylate,³⁻⁵ alkyl vinyl ketone,⁶ maleic anhydride,^{7,8} and others by radical initiators. These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.⁹⁻¹² Trisubstituted elec-

tron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with ethyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiators.¹³⁻¹⁹ The captodative (cd) olefins with geminal electron-withdrawing and electron-donating groups have a strong tendency to polymerize due to the resonance stabilization of propagating radical species, if appropriate electron-donor and -acceptor combinations in the cd substituents are chosen.^{20,21} Bifunctional monomers containing both electron-rich alkyl vinyl ether group and

electron deficient trisubstituted olefin moieties such as *p*-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate polymerize well by radical initiators.²² The question remains as to whether certain trifunctional compounds having two electron-rich alkyl vinyl ether groups and a electron-poor trisubstituted olefin moieties can be polymerized by radical initiation. To explore these problems, we have prepared a series of trifunctional monomers 2,4-di-(2-vinyloxyethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2-vinyloxyethoxy)benzylidenecyanoacetate (**2b**), 3,4-di-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**), methyl 3,4-di-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), 2,5-di-(2-vinyloxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2,5-di-(2-vinyloxyethoxy)benzylidenecyanoacetate (**6b**), and investigated their radical polymerization behaviors. This report describes synthesis and free radical polymerization of trifunctional compounds **2**, **4**, and **6**.

Experimental

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled under vacuum. Sodium iodide was dried for 4h at 100 °C under vacuum. 2,4-Dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 2,5-dihydroxybenzaldehyde were used as received from Aldrich. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Piperidine was dried with calcium hydride and fractionally distilled. α,α' -Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. γ -Butyrolactone was dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.²³

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ¹H NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min up to 700 °C was used for the thermal degradation study of polymers under nitrogen. Melting points were measured in Buchi 530 melting point apparatus and are corrected.

2,4-Di-(2'-vinyloxyethoxy)benzaldehyde (1). 2,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous

magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from *n*-butanol yielded 25.0 g (90% yield) of pure product **1**. Mp=68-69 °C. ¹H NMR (CDCl₃) δ 4.03-4.35 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.50-6.62 (m, 4H, 2 =CH-O-, aromatic), 7.82-7.86 (d, 1H, aromatic), 10.35 (s, 1H, -CHO). IR (KBr) 3100, 3082 (w, =C-H), 2954, 2875 (m, C-H), 1674 (vs, C=O), 1615 (vs, C=C), 1575 (s, C=C) cm⁻¹.

2,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (2a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 9.01 g (92% yield) of **2a**. Mp=80-81 °C. ¹H NMR (CDCl₃) δ 4.02-4.40 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.45-6.71 (m, 4H, 2 =CH-O-, aromatic), 8.17-8.34 (t, 2H, aromatic). IR (KBr) 3117, 3037 (w, =C-H), 2943, 2887 (m, C-H), 2222 (s, CN), 1611 (s, C=C), 1566 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₈H₁₈N₂O₄: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.38; H, 5.65; N, 8.46.

Methyl 2,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (2b). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 200 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 3 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 9.49 g (88% yield) of **2b**. Mp=96-97 °C. ¹H NMR (CDCl₃) δ 3.89 (s, 3H, -CO₂CH₃), 4.02-4.34 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.46-6.65 (m, 4H, 2 =CH-O-, aromatic), 8.36-8.428 (d, 1H, aromatic), 8.70 (s, 1H, aromatic). IR (KBr) 3044 (w, =C-H), 2954, 2943 (m, C-H), 2222 (s, CN), 1705 (vs, C=O), 1622, 1611, 1594, 1583 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₉H₂₁NO₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.82; N, 3.83.

3,4-Di-(2'-vinyloxyethoxy)benzaldehyde (3). Compound **3** was synthesized from 3,4-dihydroxybenzaldehyde and 2-iodoethyl vinyl ether according to the procedure similar to that of compound **1**. **3**: Mp=56-57 °C. ¹H NMR (CDCl₃) δ 4.04-4.36 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.50-6.62 (q, 2H, 2 =CH-O-), 7.01-7.06 (d, 1H, aromatic), 7.45-7.52 (d, 2H, aromatic), 9.86 (s, 1H, -CHO). IR (KBr) 3099, 3080 (w, =C-H), 2952, 2872 (m, C-H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) cm⁻¹.

3,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (4a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde **3** (5.57 g, 20 mmol) and malononitrile (1.45 g, 22 mmol) in 140 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (60 mL), water (20 mL), and cold *n*-butanol (15 mL). The obtained pale yellow

product was recrystallized from *n*-butanol to give 5.55 g (85% yield) of **4a**. Mp=64-65 °C. ¹H NMR (CDCl₃) δ 4.02-4.38 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.47-6.58 (m, 2H, 2 =CH-O-), 6.95-7.02 (d, 1H, aromatic), 7.38-7.44 (d, 1H, aromatic), 7.60-7.69 (d, 2H, aromatic). IR (KBr) 3033 (w, =C-H), 2943, 2876 (m, C-H), 2233 (s, CN), 1637, 1614 (s, C=C), 1583, 1566, 1510 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₈H₁₈N₂O₄: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.67.

Methyl 3,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (4b). Piperidine (0.085 g, 1.0 mmol) was added to a solution of 3,4-di-(2'-vinylxyethoxy)benzaldehyde **3** (5.57 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) in 140 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (60 mL), water (20 mL), and cold *n*-butanol (15 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 6.18 g (86% yield) of **4b**. Mp=86-87 °C. ¹H NMR (CDCl₃) δ 3.92 (s, 3H, -CO₂CH₃), 4.02-4.38 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.48-6.60 (m, 2H, 2 =CH-O-), 6.95-7.02 (d, 1H, aromatic), 7.47-7.54 (m, 1H, aromatic), 7.75-7.79 (m, 1H, aromatic), 8.11-8.16 (m, 1H, aromatic). IR (KBr) 3113 (w, =C-H), 2954, 2934, 2876 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1638 (s, C=C), 1591, 1519 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₉H₂₁NO₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.82.

2,5-Di-(2'-vinylxyethoxy)benzaldehyde (5). Compound **5** was synthesized from 2,5-dihydroxybenzaldehyde and 2-iodoethyl vinyl ether according to the procedure similar to that of compound **1**. **5**: Mp=55-56 °C. ¹H NMR (CDCl₃) δ 4.02-4.33 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.45-6.57 (m, 2H, 2 =CH-O-), 6.94-7.35 (m, 3H, aromatic), 10.42 (s, 1H, -CHO). IR (KBr) 3100, 3055 (w, =C-H), 2928, 2865 (m, C-H), 1673 (vs, C=O), 1615 (vs, C=C) cm⁻¹.

2,5-Di-(2'-vinylxyethoxy)benzylidenemalononitrile (6a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinylxyethoxy)benzaldehyde **5** (9.74 g, 35 mmol) and malononitrile (2.58 g, 39 mmol) in 150 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 9.37 g (82% yield) of **6a**. Mp=64-65 °C. ¹H NMR (CDCl₃) δ 3.95-4.34 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.47-6.58 (m, 2H, 2 =CH-O-), 6.92-6.98 (d, 1H, aromatic), 7.17-7.23 (m, 1H, aromatic), 7.74 (s, 1H, aromatic), 8.28 (s, 1H, aromatic). IR (KBr) 3039 (w, =C-H), 2938, 2867 (m, C-H), 2222 (s, CN), 1623 (s, C=C), 1583 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₈H₁₈N₂O₄: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.48.

Methyl 2,5-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (6b). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinylxyethoxy)benzaldehyde **5** (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 170 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was

filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 9.27 g (86% yield) of **6b**. Mp=65-66 °C. ¹H NMR (CDCl₃) δ 3.88 (s, 3H, -CO₂CH₃), 4.01-4.33 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.46-6.58 (m, 2H, 2 =CH-O-), 6.93-6.98 (d, 1H, aromatic), 7.12-7.18 (m, 1H, aromatic), 7.85 (s, 1H, aromatic), 8.73 (s, 1H, aromatic). IR (KBr) 3043 (w, =C-H), 2930, 2862 (m, C-H), 2220 (m, CN), 1735 (vs, C=O), 1625, 1617, 1594 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₉H₂₁NO₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.84; N, 3.96.

Radical Polymerizations of Monomers **2**, **4**, and **6**.

A representative radical polymerization procedure (the case of **2b**) was as follows: In a polymerization tube were placed 0.72 g (2.0 mmol) of **2b**, 1.97 mg (0.012 mmol) of AIBN, and 2.0 mL of γ -butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65 °C. After 3 h the polymerization tube was opened and the swelling polymer was poured into 300 mL of diethyl ether. The precipitated polymer was collected and dried under vacuum to give 0.68 g (94% yield) of polymer **7b**. IR (KBr) 2956, 2934, 2881 (m, C-H), 2222 (w, CN), 1727 (vs, C=O), 1611, 1580, 1508 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₉H₂₁NO₆)_n: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.81; N, 3.83. **7a**: IR (KBr) 2965, 2941, 2889 (m, C-H), 2224 (s, CN), 1616, 1561 (s, C=C), 1508 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₈H₁₈N₂O₄)_n: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.65; N, 8.51. **8a**: IR (KBr) 2936, 2887 (m, C-H), 2228 (s, CN), 1621 (s, C=C), 1583, 1517, 1508 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₈H₁₈N₂O₄)_n: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.64. **8b**: IR (KBr) 2941, 2876 (m, C-H), 2222 (w, CN), 1730 (vs, C=O), 1620 (m, C=C), 1516, 1508 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₉H₂₁NO₆)_n: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.97. **9a**: IR (KBr) 2924, 2865 (m, C-H), 2218 (m, CN), 1618 (s, C=C), 1502 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₈H₁₈N₂O₄)_n: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.63; N, 8.66. **9b**: IR (KBr) 2935, 2872 (m, C-H), 2218 (w, CN), 1740 (vs, C=O), 1620 (m, C=C), 1502 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₉H₂₁NO₆)_n: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.60; H, 5.82; N, 3.96.

Results and Discussion

Synthesis of Trifunctional Monomers **2**, **4**, and **6**.

2,4-Di-(2'-vinylxyethoxy)benzaldehyde (**1**), 3,4-di-(2'-vinylxyethoxy)benzaldehyde (**3**), and 2,5-di-(2'-vinylxyethoxy)benzaldehyde (**5**) were prepared by reaction of 2-iodoethyl vinyl ether with 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 2,5-dihydroxybenzaldehyde. Trifunctional monomers 2,4-di-(2'-vinylxyethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2b**), 3,4-di-(2'-vinylxyethoxy)benzylidenemalononitrile (**4a**), methyl 3,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**4b**), 2,5-di-(2'-vinylxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2,5-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensations of **1**, **3**, and **5** with malononitrile or methyl cyanoacetate, respectively.²⁴ Compounds **2**, **4**, and **6**

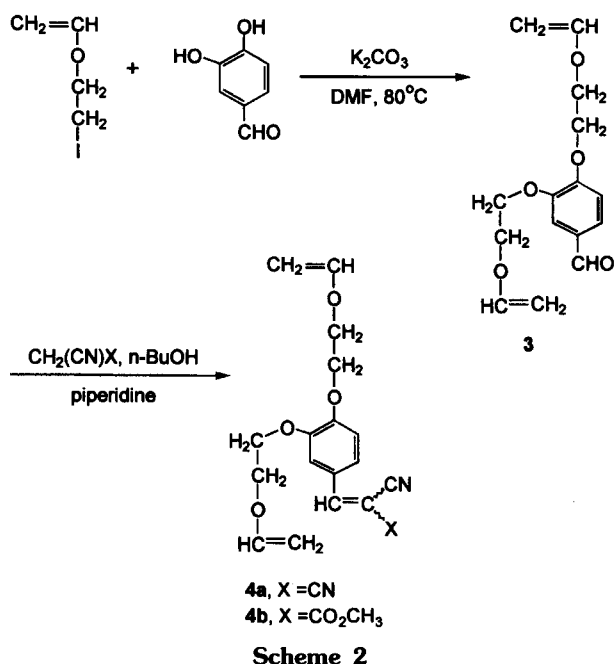
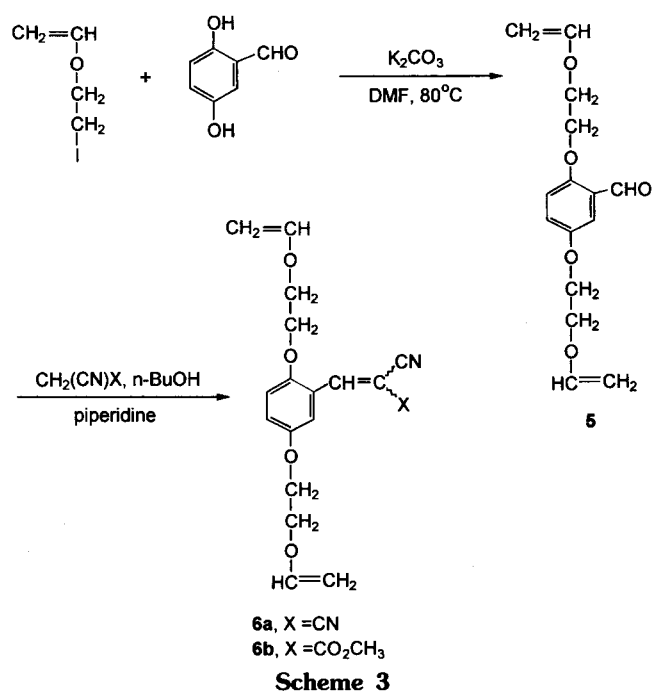
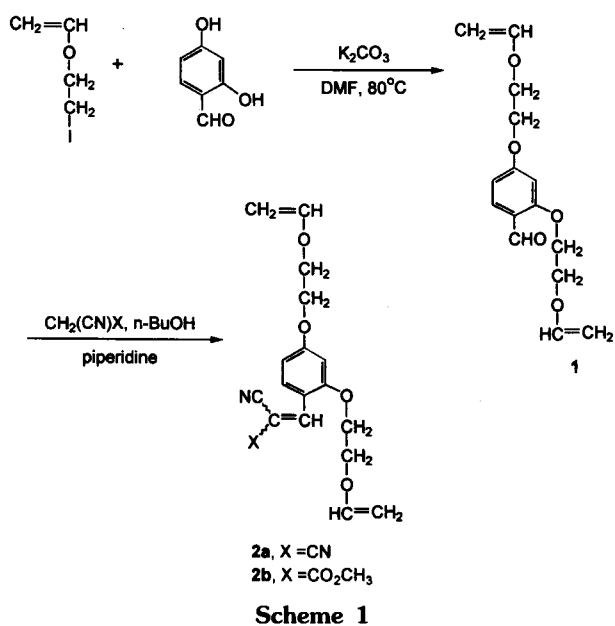


Table 1. Free radical polymerizations of **2^a**, **4^b**, and **6^c** by AIBN in γ -butyrolactone at 65 °C

Monomer	Monomer/ Solvent (mol/l L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
2a	1.00	0.6	3	75
2a	0.67	1.0	8	86
2b	1.00	0.6	3	94
2b	0.67	0.8	6	96
4a	1.00	0.6	10	56
4a	0.67	1.0	12	65
4b	1.00	0.6	5	88
4b	0.67	0.8	10	90
6a	1.00	0.6	12	71
6a	0.67	1.0	16	80
6b	1.00	0.6	6	83
6b	0.67	1.0	12	88

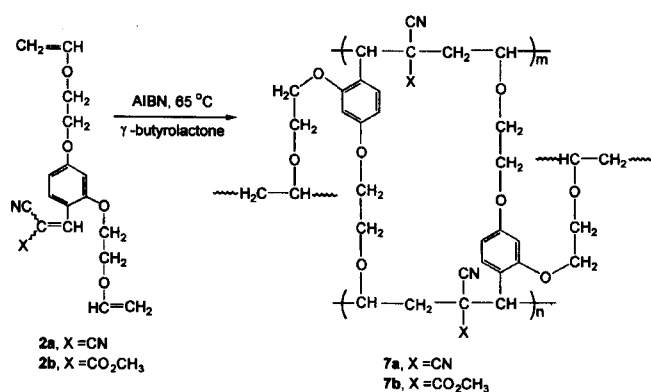
^a **2a**=2,4-Di-(2'-vinylxyethoxy)benzylidenemalononitrile; **2b**=Methyl 2,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate. ^b **4a**=3,4-Di-(2'-vinylxyethoxy)benzylidenemalononitrile; **4b**=Methyl 3,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate. ^c **6a**=2,5-Di-(2'-vinylxyethoxy)benzylidenemalononitrile; **6b**=Methyl 2,5-di-(2'-vinylxyethoxy)benzylidenecyanoacetate.

were obtained in high yield and were purified by recrystallization in *n*-butanol for polymerization. The chemical structure of the compounds was identified by proton-NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure.

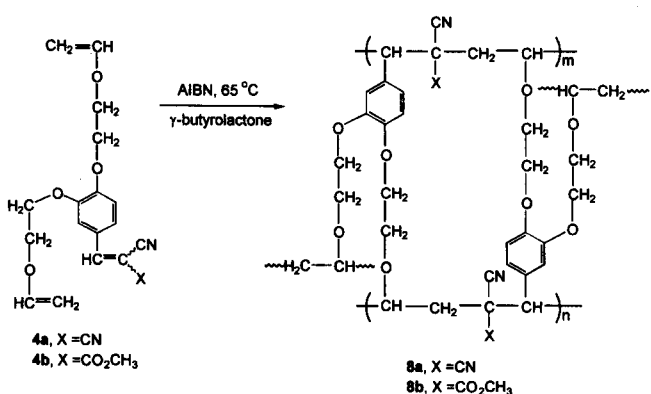
Free Radical Polymerizations of Monomers 2, 4, and 6. Trifunctional monomers **2**, **4**, and **6** were polymerized in γ -butyrolactone solution at 65 °C with AIBN as radical initiator to give polymers **7-9**. The polymerization results are summarized in Table 1. Compounds **2**, **4**, and **6** were quite reactive toward radical initiator and polymerized readily with high yields, except **4a**. Monomer **4a** gave rather lower polymer yield. The chemical structures of the polymers were identified by IR spectra and elemental analyses. The IR spectra confirmed the chemical structures, exhibiting

all the absorption bands attributable to the functional groups comprising the polymers. The trisubstituted electron-deficient benzylidenyl group participated in the vinyl polymerization, and radical polymerization of **2**, **4**, and **6** led only to optically transparent swelling polymers **7-9**. Polymers **7-9** were not soluble in any organic solvents due to cross-linking. Therefore, we have found another polymerization system that lead to highly cross-linked poly(alkyl vinyl-ethers) by free radical initiators.

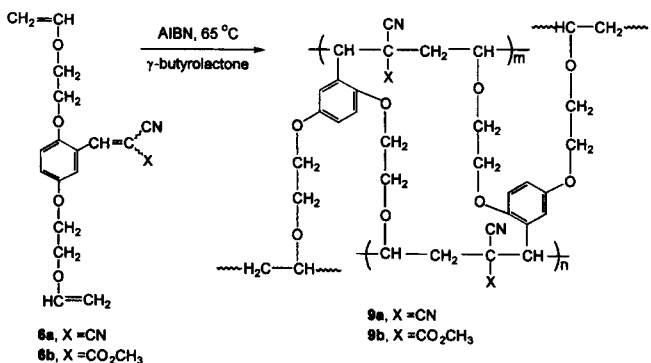
Previously we have prepared *p*-substituted bifunctional vinyl ethers containing electron acceptor olefins and poly-



Scheme 4



Scheme 5



Scheme 6

merized them with radical initiators to give highly cross-linked poly(vinyl ethers) quantitatively.²² Sterically hindered 3,5-dimethoxy-4-(2-vinyloxyethoxy)benzylidenemalononitrile did not homopolymerized by radical initiators, but it copolymerized radically with ethyl vinyl ether to give cross-linked copolymers.²⁵ Radical polymerizabilities of trifunctional divinyl ether compounds **2**, **4**, and **6** were a little lower than those of *p*-substituted bifunctional vinyl ether compounds, probably due to the steric hindrance. Compounds **2**, **4**, and **6** also polymerized well by cationic initiators such as boron trifluoride to give crosslinked poly(vinylether)s having oxybenzylidenemalononitrile or oxybenzylidenecyanoacetate, which is a NLO-chromophore.

Properties of Polymers 7-9. The polymers **7-9** were not soluble in common solvents such as methanol, ethanol, diethyl ether, benzene, toluene, acetone, methyl ethyl ketone,

Table 2. Thermal properties of polymers **7-9**

Polymer	T_g^a , °C	Degradation temp, °C ^b			Residue ^b at 700 °C, %
		5%-loss	20%-loss	40%-loss	
7a	—	285	341	375	8.0
7b	—	324	356	381	9.9
8a	—	333	356	387	16.7
8b	—	291	335	358	3.8
9a	—	273	332	362	3.3
9b	—	271	332	354	0.6

^a Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. ^b Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

cyclohexanone, dichloromethane, chloroform, DMF, and DMSO due to crosslinking. Polymers **7-9** isolated from methanol were amorphous materials. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. Polymers **7-9** showed a good thermal stability and did not decompose below 300 °C as shown in Table 2. The polymers show a double phase degradation pattern in their TGA thermograms, probably due to cross-linking. Cross-linked polymers **7-9** showed broad endothermic bands around 80-200 °C without any characteristic T_g peaks in DSC thermograms.

Conclusion

We prepared six trifunctional monomers **2**, **4**, and **6** having two electron-rich vinyl ether groups and a electron-poor benzylidenemalononitrile or benzylidenecyanoacetate moiety. The electron-deficient terminal double bond participated in the vinyl ether polymerization and radical polymerization of **2**, **4**, and **6** led to optically transparent swelling polymers **7-9** in high yields. Polymerizabilities of trifunctional divinyl ether compounds **2**, **4**, and **6** toward radical initiators were lower than those of *p*-disubstituted bifunctional derivatives due to the steric hindrance. Polymers **7-9** were not soluble in any organic solvents due to cross-linking. Polymer **7-9** showed a good thermal stability up to 300 °C in TGA thermograms. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported elsewhere.

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Solid-State ^{51}V NMR and Infrared Spectroscopic Study of Vanadium Oxide Supported on $\text{ZrO}_2\text{-WO}_3$

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Vanadium oxide catalyst supported on $\text{ZrO}_2\text{-WO}_3$ was prepared by adding the $\text{Zr}(\text{OH})_4$ powder into a mixed aqueous solution of ammonium metavanadate and ammonium metatungstate followed by drying and calcining at high temperatures. The characterization of prepared catalysts was performed using solid-state ^{51}V NMR and FTIR. In the case of calcination temperature at 773 K, for the samples containing low loading V_2O_5 below 18 wt % vanadium oxide was in a highly dispersed state, while for samples containing high loading V_2O_5 equal to or above 18 wt % vanadium oxide was well crystallized due to the V_2O_5 loading exceeding the formation of monolayer on the surface of $\text{ZrO}_2\text{-WO}_3$. The ZrV_2O_7 compound was formed through the reaction of V_2O_5 and ZrO_2 at 873 K and the compound decomposed into V_2O_5 and ZrO_2 at 1073 K, which were confirmed by FTIR and ^{51}V NMR.

Introduction

Vanadium oxides are widely used as catalysts in oxidation reactions, e.g., the oxidation of sulfur dioxide, carbon monoxide, and hydrocarbons.¹⁻⁴ These systems have also been found to be effective catalysts for the oxidation of methanol to methylformate.^{5,6} Much research has been done to understand the nature of active sites, the surface structure of catalysts as well as the role played by the promoter of the supported catalysts, using infrared (IR), X-ray diffraction (XRD), electron spin resonance (E.S.R) and Raman spectroscopy.⁶⁻⁹ So far, silica, titania, zirconia and alumina¹⁰⁻¹⁷ have been commonly employed as the vanadium oxide supports, and comparatively very few works have been reported for bi-

nary oxide, $\text{ZrO}_2\text{-WO}_3$ as the support for vanadium oxide.

It is well known that the dispersion and the structural features of supported species can strongly depend on the support. Structure and other physicochemical properties of supported metal oxides are considered to be in different states compared with bulk metal oxides because of their interaction with the supports. Solid-state nuclear magnetic resonance (NMR) methods represent a novel and promising approach to these systems. Since only the local environment of a nucleus under study is probed by NMR, this method is well suited for the structural analysis of disordered systems such as the two-dimensional surface vanadium oxide phases which is of particular interest in the present study. In addition to the structural information provided by NMR methods, the direct proportionality of the signal intensity to the number of contributing nuclei makes NMR be useful

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